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Optical Constants of Annealed a-Si:H from Transmittance at Normal Incidence

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ABSTRACT

We study changes in the optical constants of a-Si:H films caused by the thermal annealing involved in solid phase crystallization. The aim is to examine the growth mechanism, since changes in refractive index are most probably caused by a change in the network structure. The refractive index change was studied from interference fringes in transmitted light at normal incidence, and shows differing dependence on temperature in different thermal ranges. DSC measurement was also performed to examine changes in the network structure with temperature. Changes in optical and thermal properties induced by an increase of temperature reveal frequent network changes of a-Si:H below 470 °C and of a-Si in the range 470 to 570 °C. We also found crystallization at about 570 °C, and grain growth above the crystallization temperature. Knowledge of network changes in a-Si film allows orientation control by an external seed.

INTRODUCTION

Solid phase crystallization of amorphous silicon films deposited on glass substrates is a potentially useful process that has received considerable attention [1,2]. However, little is known about network changes caused by the thermal annealing that takes place with crystallization. Changes in the network structure are most likely to change the refractive index. Accordingly, we investigate changes in the optical constants of annealed a-Si:H films with a view to understanding changes in crystallization of the mother network.

Optical properties of a-Si:H films have been studied by ellipsometric measurement. Standard ellipsometry measures two relative properties of orthogonally polarized radiation. Determination of the three quantities, refractive index n, absorption coefficient α, and film thickness d, therefore requires a further independent measurement that may introduce additional errors as a result of any irregularity in the thickness. In our work, optical constants were obtained by analyzing interference fringes in transmitted light at normal incidence [3,4].

Thin a-Si:H films were deposited onto quartz substrate by PECVD. Measurements were made after isochronous annealing for 16 hours, at temperatures up to 1000 °C. The refractive index depends differently on temperature in distinct ranges; the transition temperatures between these ranges are 240, 340, 450, 570, and 680 °C. The transitions at the lowest three temperatures probably involve network changes in the a-Si:H film; the transition at 570 °C is due to crystallization of a-Si; and the transition observed above the crystallization temperature is due to grain growth. Differential scanning calorimetry (DSC) is performed to examine changes in the network structure as the temperature varies. Our demonstration that external seeding can control crystalline orientation verifies the value of transmittance analysis in detecting changes in the network.

EXPERIMENT

Undoped a-Si:H films were deposited on quartz substrates for use in transmittance measurements, and also onto crystalline silicon substrates for FTIR measurements using a parallel plate PECVD apparatus. Radio-frequency electromagnetic waves (13.56 MHz) of power 2 W (power density roughly $3.7 \times 10^{-2} \mathrm{W/cm^2}$) were used in a glow discharge of pure silane gas fed at 3.3 sccm. The chamber pressure was maintained at 10 Pa. The deposition temperature was varied from 150 to 300 °C. Film thicknesses were between 0.7 and 0.9 μm.

The hydrogen concentration C_H in the film was determined by infrared spectroscopy (FTIR-8100, Shimadzu). The integrated intensity of the Si-H stretching mode at the wavenumbers $\nu = 2000$ cm^{-1} and $\nu = 2090$ cm^{-1} were used to determine C_H [5].

Transmittance spectra of the a-Si:H thin films on a quartz substrate of thickness 0.8 mm were measured in air at normal incidence using a double beam spectrophotometer (UV-2500PC, Shimadzu). The model of the analysis used here is essentially that of Manifacier *et al.* [3], except that a rear side surface of the substrate is incorporated to allow for multiple reflection in the substrate. The three optical parameters of the film, n, α, and d, were fitted numerically [4]. The weak absorption approximation [3] was used to generate initial iteration values for n and α. An initial value for the film thickness d was obtained by interference microscopy.

An experimental transmittance (T_{exp}) curve is shown in figure 1. Envelopes of interference maxima and minima, T_{max} and T_{min}, were modeled using spline interpolation. These three independent data suffice to determine the refractive index n, the absorption coefficient α, and the film thickness d. The refractive index and the absorption coefficient based on figure 1 are shown in figures 2(a) and 2(b). Then, we can calculated transmittance T_{cal} using these optical constants, and this is also shown in figure 1. Clearly T_{exp} and T_{cal} show excellent agreement. Accuracy of the numerical calculation for n and α was checked by comparing the experimental values with the calculated results. Calculation errors were evaluated as follows. Firstly, we obtained an exact solution of the transmittance corresponding to hypothetically introduced optical constants. Then, we determined new optical constants only from the transmittance. Finally, calculation errors were obtained by
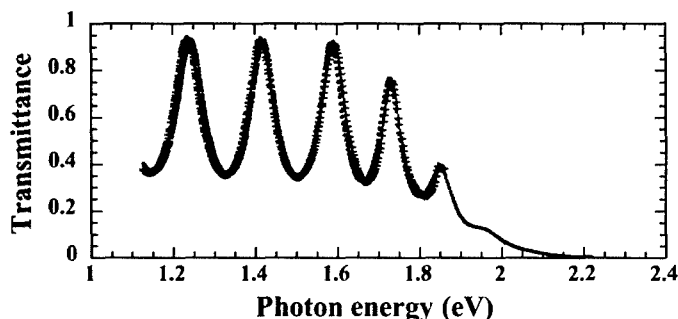

Figure 1. Transmittance of an a-Si:H film for experimental (dots) and calculated (+) values showing good agreement in the low loss region.
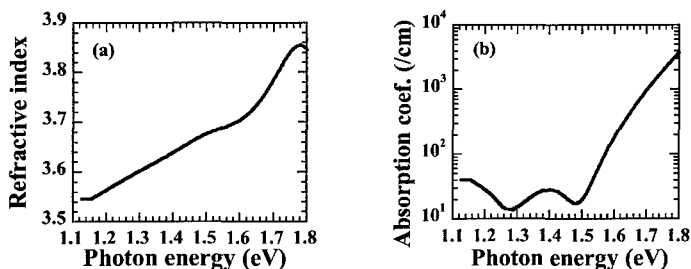
Figure 2. Optical constants for the a-Si:H film in figure 1 are shown as a function of incident photon energy; (a) refractive index and (b) absorption coefficient.

comparing the initial optical constants with newly determined ones. The calculation error for n was less than 2 % at $E = 1.15 \sim 1.85$ eV. Figure 2(a) reveals that the numerical error for n increases above $E = 1.5$ eV. We therefore determined the refractive index n at a photon energy of 1.4 eV. This is where the smallest calculation errors are expected, since the envelope curves vary slowly and the turning points of the envelopes are a long way away. Figure 2(b) shows that the numerical error for α increases in the low loss region. The error also increases in the high loss region where the interference fringes are very weak. Accuracy of the absorption coefficient was less than ± 20 % for $350 < \alpha < 4500$ cm^{-1}. We therefore define a characteristic energy E_{1500} as the photon energy for which $\alpha = 1500$ cm^{-1} so as to evaluate the loss with minimum calculation error.

Thermal analysis of the a-Si:H films was carried out by DSC, using a Shimadzu DSC-50 to assess network structure changes during annealing of the film. Samples for DSC measurements were deposited at 200 °C on quartz disks (200 μm thick, 4mm in diameter) to a thickness of about 0.48 μm. Ten samples were placed in a quartz pan with an alumina sample (0.010g) in a reference pan. The DSC module was located in a helium atmosphere (35ml/min). Samples were heated at 0.5 °C/min up to 700 °C.

It is well known that the photoinduced change of electronic properties in a-Si:H, known as the Staebler–Wronski effect (SWE), is closely related to network changes [6,7]. For SWE evaluation with temperature, a set of 10 samples were irradiated by light at 300 mW/cm^2 for 1 hour. The first DSC measurement was performed by heating the photodegraded samples to 200 °C, and the samples were annealed in the dark by maintaining them at this temperature for 30 min. The second DSC measurement up to 200 °C followed after cooling the samples to room temperature. Differences between these measurements show network changes related to the SWE. The measurement steps were repeated twice, and an accumulation was made of the difference in order to improve the S/N ratio.

RESULTS AND DISCUSSION

Variation of refractive index with temperature is shown in figures 3. Data plots are shown for both deposited and annealed a-Si:H films. The refractive index increases with temperature up to about 570 °C. Although the data points show some irregularity, the temperature variation of the refractive index can nevertheless be partitioned into several
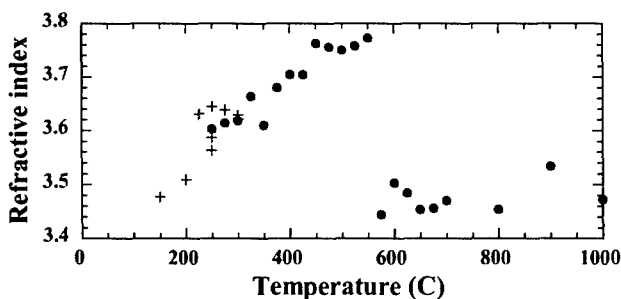
Figure 3. Refractive index of deposited a-Si:H films (+), and annealed films (●) as a function of temperature.

intervals. Approximate transition temperatures between these intervals are 240, 340, 450, and 570 °C. A weak dependence of the refractive index on temperature is observed in the ranges 240−340 and 450−570 °C, but a strong dependence in the other intervals. These changes seems to be caused by changes in the mother network.

The hydrogen concentration (C_H) measurement indicates that C_H decreases as the temperature increases, and reaches zero at about 475 °C. The transition temperatures at 240, 340, and 450 °C are therefore most probably due to network changes of the a-Si:H. Our PECVD apparatus gave device-quality a-Si:H films at a deposition temperature of about 240 °C, which is very close to the lowest critical temperature. Device-quality films relate to their defect density [8]. The present result indicates that the defect density can be related to network changes.

Variation of the characteristic energy E_{1500} with temperature is shown in figure 4(a). Data for deposited and annealed films are again both plotted in the figure. The same critical temperatures as shown in figure 3 are seen in figure 4(a). Since the turning points are not clear in this figure, however, data points up to 500 °C are plotted in figure 4(b) as a function of hydrogen concentration. The transition temperatures of 240, 340, and 450 °C correspond to critical hydrogen concentrations of about 15, 10, and 5 atomic %. It is seen
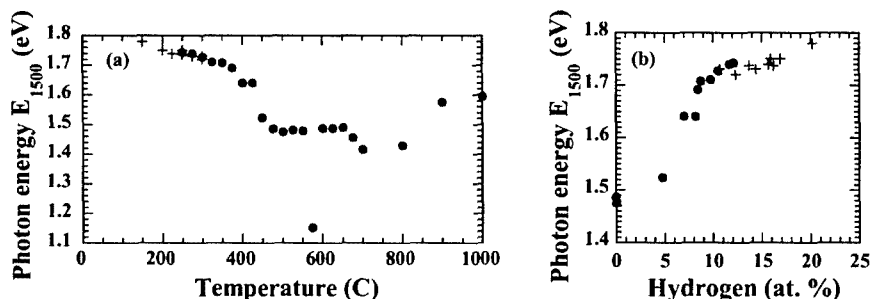

Figure 4. Change of photon energy E_{1500} with (a) temperature, and (b) hydrogen concentration. Data plots are shown for both deposited films (+), and annealed films (●).
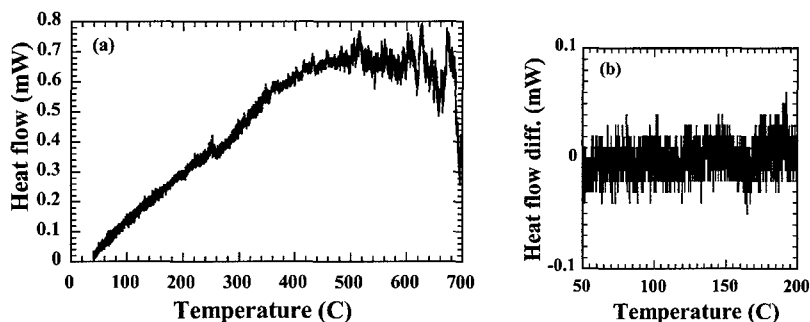
Figure 5. (a) DSC spectrum of a-Si:H films deposited at 200 °C and (b) accumulated heat flow difference between a-Si:H films with and without photoinduced network changes.

that the absorption properties of a-Si:H change at the critical temperature.

The sudden change at 575 °C in figures 3 and 4(a) is most probably caused by a crystallization. Nano-crystals reduce the refractive index and make the film opaque. Since a narrow range in particle size is responsible for the strong absorption, a low E_{1500} value is seen in a narrow temperature range in figure 4(a). The XRD spectrum of annealed films also indicated crystallization at above 570 °C. The turning points in figures 3 and 4 at above 570 °C therefore show grain growth.

Changes in the mother network in the annealed film with temperature were investigated using DSC measurements. A typical DSC spectrum is shown in figure 5. The exothermic spikes above $\sim 570°$C are most probably caused by grain growth, and those below the crystallization temperature by a network change in the a-Si (around 470 and 570 °C) or a-Si:H (below 470 °C). A different DSC spectrum was observed for each measurement; however, several exothermic peaks were observed at similar temperatures: 225−250, 417, 560, 575, 610, and 670 °C. The exothermic peak at 225−250 °C varies from run to run but is the largest signal around 240 °C. Since this characteristic temperature is almost the same as that observed in figures 3 and 4, the thermal characteristics also support the hypothesis that fabrication of device-quality a-Si:H film depends on network changes. Small signals at 560 and 575 °C presumably correspond to the crystallization that generates sharp changes in optical properties as shown in figures 3 and 4. The larger signals at temperatures above the crystallization temperature in figure 5(a) most probably correspond to the growth of larger grains. The exothermic peak at 670 °C appears to correspond to the critical temperature of 680 °C in figures 3 and 4. The accumulated heat flow difference is indicated in figure 5(b). Exothermic peaks located in a range of 190−192 °C are enhanced by the accumulation. These peaks therefore correspond to the SWE.

Frequent change in the network is observed in figure 5(a) even though the temperature is well below the crystallization threshold. This suggests a possible means of control of the crystalline orientation in the film if the film is in contact with a seed crystal. Accordingly, isothermal annealing was performed with a (100)-oriented Si wafer at about 560 °C. The XRD spectrum of the film is shown in figure 6. It is well known that a crystallized a-Si film shows (111), (220) and (311) peaks in its XRD spectrum, but no (400) peak. The (400) peak in figure 6 is clearly caused by the (100)-oriented seed crystal.
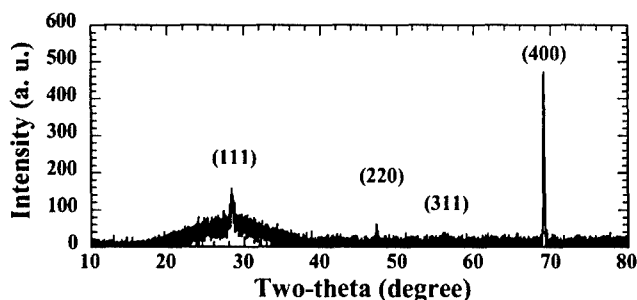
Figure 6. XRD spectrum of annealed a-Si film. The sample was maintained in contact with a (100) seed crystal during annealing.

CONCLUSIONS

We have studied changes in the Si network structure in annealed a-Si:H films from their optical and thermal properties. Optical properties were obtained from interference fringes in the transmittance at normal incidence, and thermal properties by DSC. The optical properties show differing temperature dependence in distinct temperature ranges. The transition temperatures of 240, 340, and 450 °C between these ranges correspond to network changes in a-Si:H; at 570 °C to crystallization; and at 680 °C to grain growth. The thermal properties indicate more transition temperatures arising from network changes. We highlight the fact that the SWE is related to network changes in the range 190 − 194 °C, and that the fabrication of device-quality a-Si:H film is related to a network change at around 240 °C. Finally, successful solid-phase seeding has been demonstrated, stimulated by network changes in a-Si films at temperatures around 475 and 570 °C.

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